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TEMPERATURE EFFECT ON INDUCED INFRARED ABSORPTION IN GASEOUS ACETYLENE AT PRESSURE*

BY KUNIO OZAWA

Introduction

The influence of intermolecular interaction on the infrared absorption spectra of molecule is not only dependent on the kind of absorbing and foreign molecules, but also on the phase state, density and temperature of the molecule¹⁻⁴⁾. Especially in the infrared spectra of compressed gas, the pressure-induced absorption band corresponding to the infrared forbidden transition is observed and the frequency of this vibration will be the same as the Raman frequency corresponding to this molecular vibration, that is, in compressed gas a break-down of the infrared selection rules takes place. These phenomena may be interpreted by assuming that the electronic charge distribution over the molecule is altered by induction and distortion during the close collisions of the gas molecules at high pressure, so that a molecular vibration, which takes place without a variation of the dipole moment comes to be the vibration with a variation of the dipole moment.

We already observed⁵⁾ that in gaseous acetylene at high pressure the totally symmetric stretching vibration ν_2 -band at 1974cm^{-1} which was infrared-inactive was rendered the infrared-active absorption band, and also investigated the effect of density and polarizability of the foreign gases on the induced band.

In the present investigation the effect of temperature on the pressure-induced absorption ν_2 -band of compressed gaseous acetylene at 11.8 and 4.0 Amagat densities has been studied in the range of temperature from 20 to 240°C , and the rotational constant, B value, of acetylene molecule has been obtained from the frequency separation of the Q_P and Q_R submaxima on the induced absorption band, $\Delta\nu_{Q_P Q_R}^{\text{max}}$. Furthermore, for acetylene polymers which were produced at high pressure and high temperature, the infrared spectra have been measured and also discussed.

Experimentals

The optical windows of the high pressure absorption cell with 14.8cm path length were the LiF crystals of 1.2cm in thickness and 1.9cm in diameter. The pressure-tight windows whose

* This investigation has been done by K. Ozawa, being in the post-graduate course, under the direction of Prof. R. Kiyama.

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- 2) R. Coulon, L. Galatry, J. Robin and B. Vodar, *Disc. Farad. Soc.*, **22**, 22 (1956)
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- 4) D. A. Chisholm, W. F. J. Hare et H. L. Welsh, *J. Phys. et Rad.*, **15**, 511 (1954)
- 5) E. J. Allin, W. F. J. Hare and R. E. MacDonald, *Phys. Rev.*, **98**, 544 (1955)
- 6) R. Kiyama, S. Minomura and K. Ozawa, *Proc. Japan Acad.*, **30**, 753 (1954)
- 7) S. Minomura, *This Journal*, **24**, 49 (1955); **26**, 9, 41 (1956)

construction is shown in Fig. 1 was designed by Bridgman's principle of unsupported area. The Teflon gaskets were employed to prevent the leakage due to the difference of the coefficients of expansion between the LiF window and the supporting plug at high temperature. The perforated steel cap, C, which was screwed outside the supporting plug, P, was also useful for holding the window in position when the cell was evacuated. The absorption cell was heated by an electrical furnace so wound that even at the highest temperature 240°C the central part of the absorption cell, about 14cm long, was kept at uniform temperature with the fluctuation in less than 2°C.

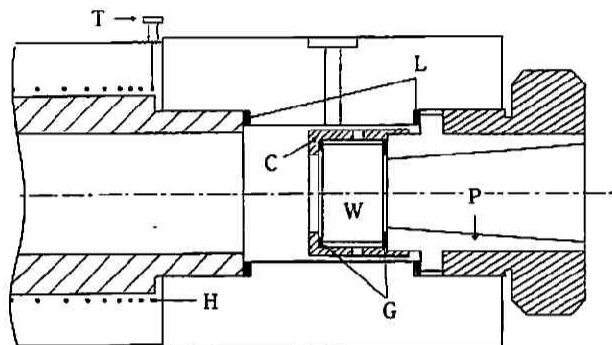


Fig. 1 The pressure proof optical window mounting to the absorption cell

- W : LiF window
- P : supporting plug
- C : steel cap
- G : Teflon gasket
- L : aluminium gasket
- H : electric heater
- T : terminal

The measurements of the spectra were carried out with a Hilger D-42 infrared spectrometer equipped with a NaCl prism and FT-16 Hilger vacuum thermopile. For the spectrum of the acetylene polymers in the longer wavelength region, a Beckman IR-2 infrared spectrometer using a KBr prism was also employed. The purification of gaseous acetylene and the data for the calculation of Amagat density were described in the previous papers⁵⁾.

The measurements of the optical density, $\log(T_0/T)$, were carried out over the wavelength range $4\sim 6\mu$ after the gas had reached thermal equilibrium at a certain temperature. In this expression T_0 and T are the intensities of light transmitted through argon at 1 Amagat and compressed gaseous acetylene at the same temperature respectively, and then the infrared radiation emitted from the absorption cell at high temperature is compensated.

Infrared measurements of the acetylene polymers were carried out on the following two cases.

- (1) The polymers of yellow amorphous state, which were deposited on the KCl crystal plate



Photo. Microphotograph of the acetylene polymers deposited on the KCl crystal plate which is the lower dark part in Photo. ($\times 200$)

($25 \times 25 \times 3 \text{ mm}^3$) sealed together acetylene by heating the gaseous acetylene of about 10 Amagat at 240°C for 10 hours in the autoclave, were measured over the wavelength range of $4 \sim 25 \mu$. (2) The polymers, which were deposited on the LiF windows of absorption cell by heating acetylene of 11.8 Amagat at 240°C , were measured over the range $4.5 \sim 6 \mu$. The absorption of fresh crystals of the same thickness were used as the back-ground. The microphotograph of the acetylene deposited on the KCl crystal plate is shown in Photo.

Experimental Results

For respective temperatures, 20, 120, 180 and 240°C , the absorption contours of the pressure-induced ν_2 -band of acetylene at 11.8 Amagat density are reproduced in Fig. 2. The position of ν_0 (1974 cm^{-1}), band origin⁶⁾, and the submaxima of ν_2 -band, Q_P and Q_R , are marked in this figure. Each of the spectra shows that the band breadth and the separation of Q_P and Q_R increase as the temperature increases. The temperature effect up to 180°C on the peak height is small.

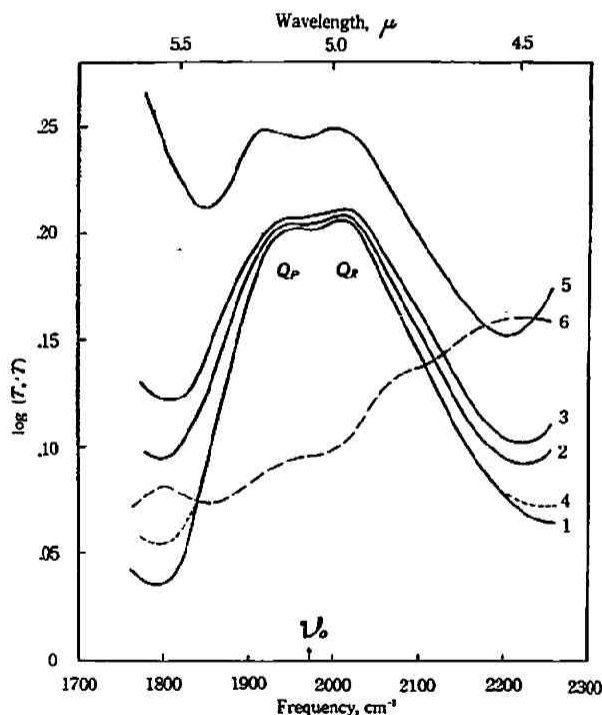


Fig. 2 The effect of temperature on the induced ν_2 -band for 11.8 Amagat acetylene

- Curve 1 at 20°C
 2 at 120°C
 3 at 180°C
 4 at 20°C after heat treatment at 180°C
 5 at 240°C
 6 acetylene polymers

After a measurement at 180°C , the remeasured spectrum of acetylene being cooled down to 20°C gives rise to the discrepancies at the band tails which are shown by dotted Curve 4 and suggests the faint existence of polymer products on the optical windows. On the other hand, an anomaly observed in the spectrum at 240°C is due to the absorption and the scattering of

6) G. Herzberg, *Molecular Spectra and Molecular Structure*, D. van Nostrand Co., Inc., p. 288 (1945)

acetylene polymers, which is produced on the surface of the optical windows, in addition to the induced absorption of gaseous acetylene. The broken Curve 6 in Fig. 2 is a spectrum in the same region of wavelength, after the gas in the cell is evacuated, for the polymers deposited on the LiF windows.

In Fig. 3 the half breadth, $\Delta\nu_{\frac{1}{2}}$, and the separations of the Q_P and Q_R submaxima, $\Delta\nu_{Q_P Q_R}^{max}$, for acetylene of 11.8 Amagat at temperatures 20, 120 and 180°C are plotted against the square root of absolute temperature, $T^{\frac{1}{2}}$. These values show a straight line through the origin, and

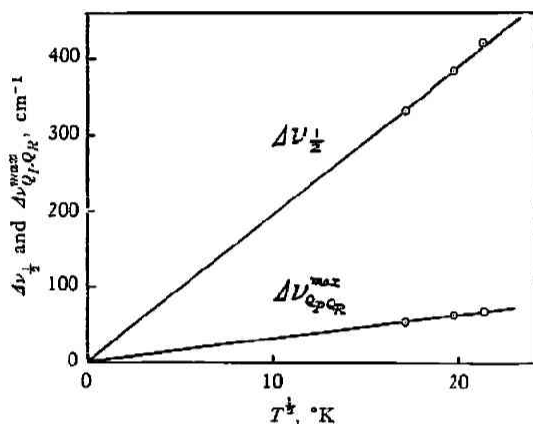


Fig. 3 The dependences of $\Delta\nu_{\frac{1}{2}}$ and $\Delta\nu_{Q_P Q_R}^{max}$ on $T^{\frac{1}{2}}$ for the induced ν_2 -band of 11.8 Amagat acetylene

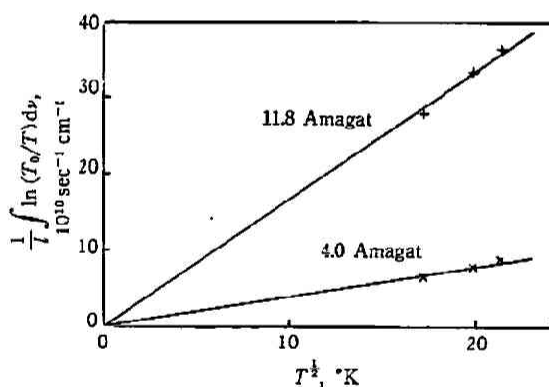


Fig. 4 The dependence of $\frac{1}{T} \int \ln(T_0/T) d\nu$ on $T^{\frac{1}{2}}$ for the induced ν_2 -band of 11.8 and 4.0 Amagat acetylene

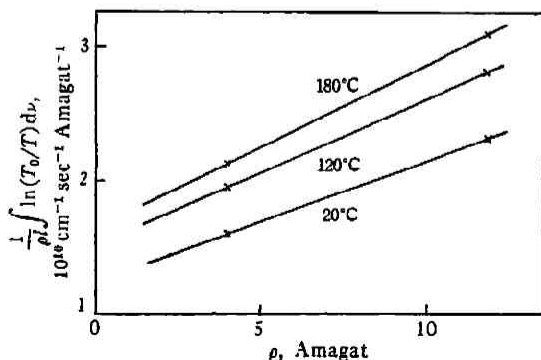


Fig. 5 The dependence of $\frac{1}{\rho} \int \ln(T_0/T) d\nu$ on ρ for the induced ν_2 -band of acetylene at various temperatures

the $T^{\frac{1}{2}}$ dependences on the band breadth and the submaxima separation are recognized. Although the temperature effect on the acetylene of 4 Amagat, since the absorption intensity of it is small, is not so prominent as one of 11.8 Amagat, the same relationship is observed.

In Fig. 4 the integrated absorption coefficients, $\frac{1}{T} \int \ln(T_0/T) d\nu$ ($\text{sec}^{-1} \text{cm}^{-1}$) of the ν_2 -band of acetylene for both densities of 4.0 and 11.8 Amagat are plotted against the square root of absolute temperature, $T^{\frac{1}{2}}$. In these cases also, the $T^{\frac{1}{2}}$ dependences are recognized.

On the other hand, from the linearity between the absorption coefficient, $\frac{1}{\rho l} \int \ln(T_0/T) d\nu$ ($\text{sec}^{-1} \text{cm}^{-1} \text{Amagat}^{-1}$) and density, ρ which has been described in the previous papers⁵⁾, the density effect on the absorption coefficient at various temperatures is shown in Fig. 5.

The infrared spectrum of the gas phase being cooled down to 20°C after the heat treatment at 240°C, was entirely identical with the original gaseous acetylene, so that in the gas phase the dimer like as vinylacetylene being the lower boiling compounds were not found. The measurements of infrared absorption intensity of $\nu_4 + \nu_5$ -band (1328cm^{-1}) whose intensity had been investigated in the previous papers⁵⁾, gave also the same value for both gases.

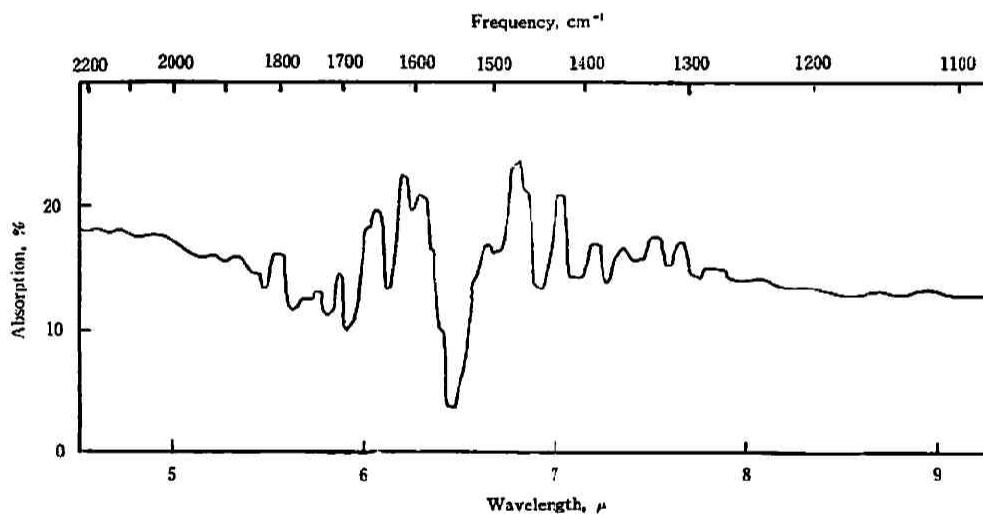


Fig. 6 The infrared spectrum of acetylene polymers produced at 240°C and 10 Amagat

The polymerization of acetylene will be considered to begin from about 180°C, and on the surface of the optical windows the production of the viscous and colorless liquid was observed from about 200°C. These polymers changed to the higher polymers of the pale yellow amorphous state with the lapse of time. In Fig. 6 the infrared spectrum of acetylene polymers deposited on the KCl plate is given. This spectrum shows the marked absorption contour in the range $5.5 \sim 8 \mu$ and indicates the scattering due to the uneven grain sizes of the acetylene polymers over the whole frequency range $4 \sim 25 \mu$.

Considerations

It is definitely shown from Figs. 2~4 that the band breadth and integrated absorption coefficient of the pressure-induced absorption ν_2 -band of acetylene would be proportional to the square root of absolute temperature, and that the peak height of the absorption band depends very strongly on the density. The effect of temperature is small for the peak height. These results are in good agreement with Kranendonk's theory⁷⁾ in which he proposed the hypothesis that the pressure-induced absorption was due to the dipole moment mainly by the overlap force operated during a close binary collision, and also predicted that the band breadth would be proportional to $T^{\frac{1}{2}}$. On the other hand, the $T^{\frac{1}{2}}$ dependence on the breadth of the pressure-induced band was also confirmed by the experimental results of Welsh *et al.*^{3,4,8)} on the pressure-induced 0-1 vibrational band of molecular hydrogen. Namely the band breadth is due to the fact that the absorption can take place only during the short time of interaction at a collision, and since this time is inversely proportional to the molecular velocity, the corresponding breadth for one collision is proportional to the molecular velocity. It finally comes to be expected that the band breadth will be proportional to $T^{\frac{1}{2}}$.

The rough rotational constant, B value, may be obtained from the following formula for the separation of submaxima of the linear molecule⁹⁾,

$$\Delta\nu_{Q_P Q_R}^{max} = \sqrt{\frac{8kBT}{hc}} = 2.358 \sqrt{BT},$$

where

$$B = h/8\pi^2 c I_B,$$

I_B = the moment of inertia about an axis
perpendicular to the molecular axis,

h = Planck's constant,

c = velocity of light,

k = Boltzmann's constant,

T = absolute temperature.

Assuming that the submaxima separation of the pressure-induced band of acetylene should follow the formula described above, we may obtain the B value, the rotational constant of ν_2 -band of acetylene corresponds about 1.4 cm^{-1} from the slope of the straight line which shows the proportionality between $\Delta\nu_{Q_P Q_R}^{max}$ and $T^{\frac{1}{2}}$. This B value is a satisfactory value in comparison with the B value, 1.17 cm^{-1} which Welsh *et al.*¹⁰⁾ have recently given by investigating the Raman spectra of acetylene at an atmospheric pressure with high spectrographic dispersion.

The absorption coefficient of ν_2 -band for acetylene at each temperature is determined from

7) J. van Kranendonk, *On the Theory of Pressure-broadening and Pressure-induced Absorption*, Univ. Amsterdam (1952)

8) M. F. Crawford, H. L. Welsh, J. C. F. MacDonald and J. L. Locke, *Phys. Rev.*, **80**, 469 (1950)

9) G. Herzberg, *Molecular Spectra and Molecular Structure*, D. van Nostrand Co., Inc., pp. 13, 391 (1945)

10) T. Feldman, G. G. Shephard and H. L. Welsh, *Can. J. Phys.*, **34**, 1425 (1956)

the slopes of the $\frac{1}{\rho l} \int \ln(T_0/T) d\nu \sim \rho$ isotherms. These values are given in the following Table.

Table Absorption coefficient of the induced ν_2 -band for acetylene at various temperatures

Temp. °C	Absorption coefficient $10^9 \times \text{sec}^{-1} \text{ cm}^{-1} \text{ Amagat}^{-1}$
20	0.92
120	1.11
180	1.21

Concerning the mechanism of the polymerization caused from the thermal treatment of compressed acetylene, a number of theories^{11,12)} have been presented. It is considered that the viscous and colorless liquid polymers produced with rising temperature of compressed acetylene would be the unsaturated aliphatic compounds as the trimers (C_6H_6), divinylacetylene etc., and the tetramers (C_8H_8) being the liquid chemically similar to the trimers. These lower polymers are converted by increasing the degrees of polymerization into the high polymers being of pale yellow amorphous states. Although the infrared spectrum of acetylene polymers in Fig. 6 shows the scattering due to the uneven grain sizes over the whole range of frequency, this spectrum indicates that the peaks near 1600cm^{-1} may correspond to the mode of $-\text{C}=\text{C}-$ stretching and the peaks in the range of $1500\sim 1400\text{cm}^{-1}$ the mode of $-\text{CH}_2$ bending¹³⁾. On the other hand, the rising of the temperature of the autoclave up to 180°C , in which these acetylene polymers exposed in the air for a few days were sealed together with acetylene of 10 Amagat, gave rise to the explosion of acetylene whose pressure corresponded to about more than 1500 atm. This explosion may be probably due to the oxygen combined with the acetylene polymers and also supported by McLennan *et al.*'s report¹⁴⁾ that by the action of cathode rays acetylene was polymerized to the ciliated yellow amorphous solids, which took up about 30 per cent of its weight of oxygen on standing in air and were highly unsaturated.

The author has great pleasure in expressing his sincere thanks to Prof. Ryo Kiyama for his advice and encouragement throughout the course of this investigation. He also wishes to express his hearty thanks to Mr. Shigeru Minomura for his kind co-operation extended to him and for taking part in the discussion on many occasions. He is also indebted partly to the Department of Education for the Grant in Aid for Fundamental Scientific Individual Research (The Physico-Chemical Researches on Acetylene) shared out to Prof. Ryo Kiyama.

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